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Supporting information for the article:

On the origin of fluorescence emission in optically non-linear DCNP crystal

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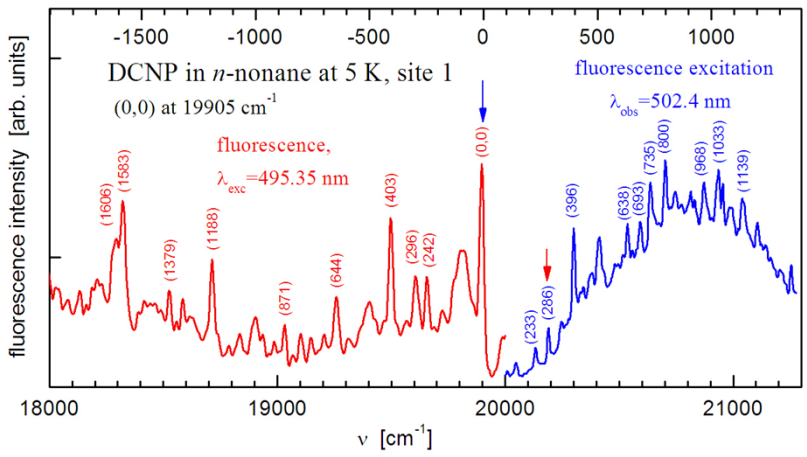
1. Fluorescence and fluorescence excitation spectra of main sites occupied by DCNP molecules in *n*-nonane matrix at 5 K.



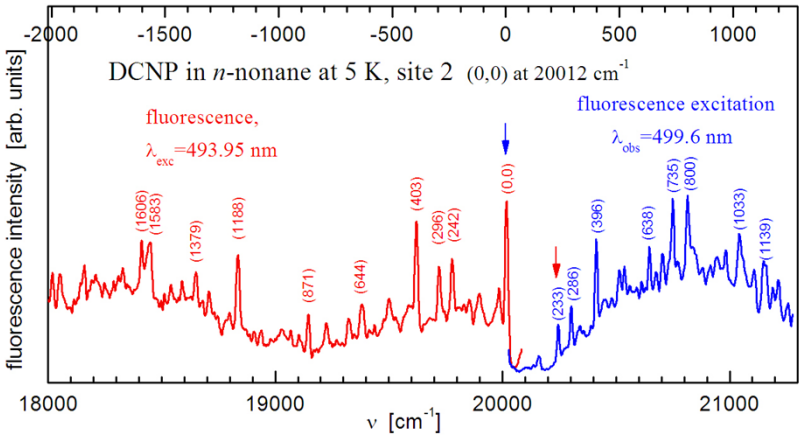


Figure S1. Fluorescence (red lines) and fluorescence excitation (blue lines) of the two main sites occupied by DCNP molecules in *n*-nonane Shpol'skii matrix. Blue arrows indicate the (0, 0) transition lines in the fluorescence spectrum of the sites, red arrows show excitation wavelength which were used when recording the fluorescence spectra. Numbers in parentheses indicate vibrational frequencies (given in cm^{-1}) calculated in respect to the (0, 0) origin lines. Spectra were not corrected for spectral sensitivity of a detection system (fluorescence) and for spectral distribution of intensity of an exciting dye laser (fluorescence excitation).

2. Absorption polarization spectra of a single DCNP crystal at 5 K.

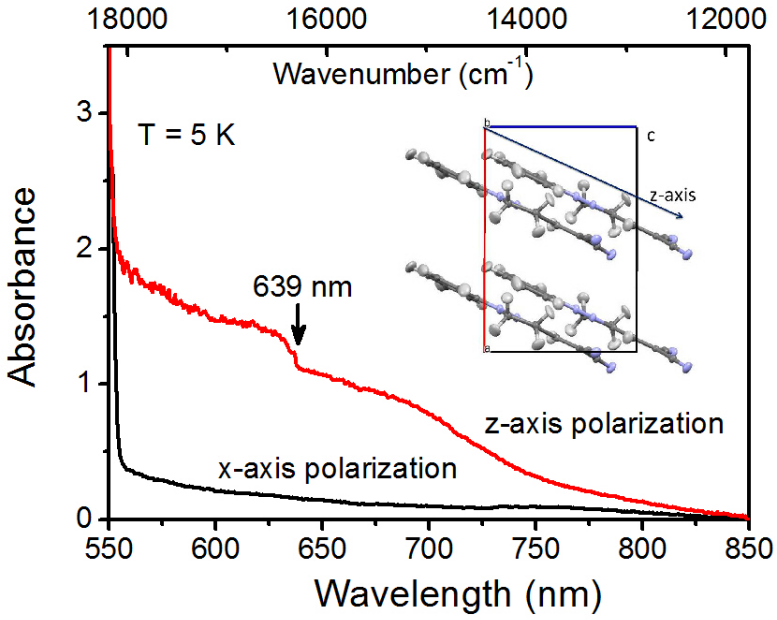


Figure S2. Absorption spectra recorded at 5 K for a thick (thickness about 2.5 mm) single crystal of DCNP, observed below the absorption edge at 552 nm for two, perpendicular, polarizations. Arrow points to the step-like decrease of the absorption at 639 nm. Inset: Projection of the unit cell along the b-axis (taken from the neutronographic data [12]). The z-axis is directed along the long DCNP molecular axis. Spectra corrected on light reflection from the crystal face at the z-axis light polarization with $n_z \approx 2.7$ at 633 nm give absorption coefficient α_z (633 nm) = 11 cm^{-1} and for α_x(633 nm) $\approx$ 2 cm^{-1} assuming $n_x = 1.9$.

3. Raman spectrum of DCNP single crystal

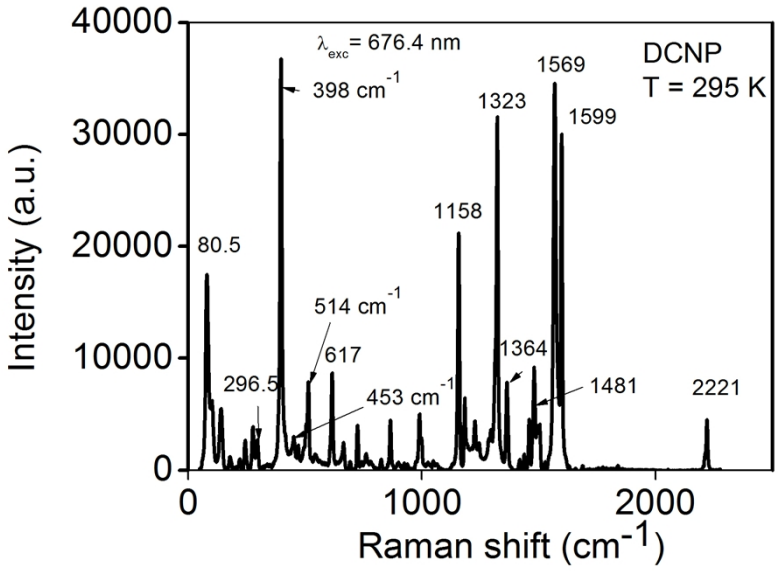


Figure S3. Raman spectrum of DCNP single crystal taken at T = 295 K using λ_R = 676.4 nm. The fluorescence background has been numerically cut off.

4. Calculated and experimentally determined vibrations in DCNP crystals

Table 1. Frequencies of vibrations calculated for isolated (in vacuum) DCNP molecules in their electronic ground state (frequencies are multiplied by factor 0.95 in order to better match with the experimental values) and their attribution to experimentally determined frequencies of vibrations observed in the fluorescence (recorded at 5 K) and Raman (at 295 K) spectra of single crystals of DCNP and in fluorescence spectrum of DCNP molecules isolated in *n*-nonane matrix (at 5 K). All frequencies are given in cm^{-1}. Intensities of the lines are given in parentheses.

Calculated frequencies (×0.95)	fluorescence spectrum in crystal	Raman spectrum in crystal	fluorescence in *n*-nonane matrix	Assignment

31.2 (0.12)				
36.2 (0.19)				
65.6 (0.36)				
73.0 (0.3)		80 (17504)		
99.5 (0.04)		102 (6322)		
109.4 (0.89)				
120.8 (1.19)				
140.7 (0.11)		140.5 (5528)		
207.7 (0.8)		220.9 (966)		
229.0 (0.33)		244 (2633)	242	in-plane waging
261.5 (0.16)		277.6 (3908)		
277.6 (0.54)	285.3		296	in-plane bending
374.7 (0.18)		397.8 (36786)		
397.5 (0)		417.7 (2925)	403	phenyl out of plane
440.1 (0.19)	438.5	451 (3034)		CCN bending
453.5 (0.06)	453	471.7 (2191)		CN out of plane
490.6 (0.05)				
492.2 (1.22)		514.4 (7908)		
507.6 (0.01)				
583.5 (0.09)		616.7 (8708)		
594.4 (0.13)				
615.2 (1.21)				
644.2 (9.75)			644	phenyl in-plane
669.3 (3.72)		666.1 (2368)		
696.9 (0.77)	698.7	693 (717)		pyrazole in-plane
732.0 (6.7)	715	725.3 (4004)		phenyl CH out of plane

760.2 (5.27)		761 (1441)		pyrazole in-plane
789.1 (0)				
798.7 (0.03)		825 (919)		
833.8 (2.64)		866 (4483)	871	pyrazole stretching
865.8 (0.19)				
867.3 (0.6)				
901.0 (1.24)				
933.3 (0.01)				
954.6 (0.02)				
956.8 (0.63)		990.8 (5056)		
957.1 (0.03)				
984.9 (0.07)				
998.6 (0.03)				
1002.0 (1.06)				
1050.3 (2.28)		1158 (21186)		
1111.9 (0.13)				
1115.6 (0.66)				
1117.8 (0.38)				
1134.2 (1.21)				
1158.8 (100)		1184.7 (6458)	1188	NN stretching
1184.1 (0)				
1200.6 (50.71)		1228.4 (4394)		CC stretching / CH2 bending
1244.5 (18.24)	1246.6	1296 (3647)		CH bending
1270.6 (2.85)				
1274.1 (0.16)				

1293.9 (4.96)				
1325.1 (42.01)	1342.8	1323.4 (31606)	1324	CH_2 bending
1375.7 (30.7)			1379	CN / CC stretching
1381.8 (4.75)				
1412.8 (5.48)				
1420.4 (19.87)				CH_2 scissors
1448.8 (86.01)	1447.8	1504.6 (4119)		phenyl CH bending
1465.7 (58.84)	1495	1569.5 (34592)		pyrazole CN stretching
1538.7 (68.65)	1561,2	1598.7 (30052)	1583	CC stretching
1551.9 (1,72)				
1566.9 (8.3)			1606	phenyl CC stretching
2109.7 (4.1)				
2213.6 (23.17)		2221 (4524)		CN stretching

TOC – graphical abstract